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(54) PROCESS FOR MAKING FLEXIBLE POLYURETHANE FOAM

VERFAHREN ZUR HERSTELLUNG VON FLEXIBLEM POLYURETHANSCHAUM

PROCEDE POUR FABRIQUER DE LA MOUSSE DE POLYURETHANE SOUPLE

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(56) References cited:
EP-A- 0 043 110
EP-A- 0 092 700
FR-A- 2 128 582

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Description

The present invention relates to a process for making flexible polyurethane foam. In particular, the present invention relates to a process for making conventional "hot-cure" flexible polyurethane foams having improved breathability.

Flexible polyurethane foam is a known material and is widely used for making bedding, furniture cushions and seating. Such foam is conventionally prepared by a "hot-cure" process in which the foam, when fully risen, is heated at an elevated temperature e.g. 130-150°C, in order to effect its cure. The manufacture of such foams has previously involved the use of silicone surfactants of high molecular weight to stabilise the foam.

A problem arises when such surfactants are used to produce low density foam. Low density foam requires the use of high levels of silicone surfactant to stabilise the foam. Unfortunately the use of high levels of silicone surfactant produces cells in which the openness of the foam cells is low. As a result such foams are slow to recover after compression, i.e. they exhibit poor breathability.

It has now been found that when a high molecular weight silicone surfactant (MW typically in the range 10,000-20,000) is replaced by a silicone surfactant mixture comprising a minor amount of a low molecular weight silicone surfactant and a major amount of a high molecular weight surfactant, the breathability of the foam produced at a given silicone surfactant level is improved.

Accordingly, the present invention provides a process for preparing flexible polyurethane foam which process comprises reacting and foaming a foam formulation comprising

(1) a polyol selected from a polyether polyol or a polymer polyol wherein the polyol is one having an average functionality in the range 2 to 6 and in which less than 20% of the hydroxyl groups are primary hydroxyl groups,
(2) an isocyanate composition containing toluene diisocyanate,
(3) a catalyst for the polyurethane forming reaction, and
(4) a blowing agent
characterised in that the foam formulation further comprises a silicone surfactant composition which comprises a mixture of

(a) between 5 and 20 cut % of a lower molecular weight silicone surfactant having the formula

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_x(Si(CH_3)(R^2)O)_ySi(R^1)_3$$

wherein

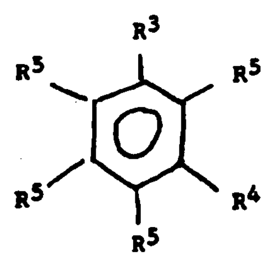
(i) x and y are such that

$$x+y = 2 - 10$$

and

$$\frac{y}{x+y} = 0.1 - 0.5$$

(ii) the R^1 groups are independently selected from C_1 to C_{10} hydrocarbyl groups
(iii)the R^2 group are independently selected from groups having the generic formula



wherein R^3 is a divalent hydrocarbyl group; R^4 is a polar group selected from -OH, -NH_2, Cl, Br, and CH_2OH and the R^5 groups are independently selected from hydrogen or C_1 to C_{10} alkyl or alkoxy groups and

(b) between 95 and 80 wt % of a high molecular weight silicone surfactant having the formula

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_p(Si(CH_3)(R^6)O)_qSi(R^1)_3$$

wherein

(i) p = 40 - 150

(ii) q = 3 - 15
(iii) R^6 is an ethylene oxide/propylene oxide copolymer having a molecular weight in the range 1500 - 5000 capped with alkoxy at one end and bound to silicon by a divalent hydrocarbyl group.

the molecular weight of the high molecular weight silicone surfactant being in the range 10,000 to 50,000.

As regards the low molecular weight silicone surfactant, this is preferably one in which the R^1 group is a methyl group and wherein x + y is between 6 and 10. It is also preferable that the R^2 groups are ones where R^4 is a hydroxyl or oxygen containing group.

The high molecular weight silicone surfactant is preferably one of the readily available silicone surfactants which are used in hot-cure foam formulations. It is preferred to use such a silicone surfactant in which the R^1 groups are methyl groups and p and q are respectively in the ranges 60 - 80 and 5 - 9.

The other components of the hot-cure foam formulation are well known to those skilled in the art. The polyol, for example, is either a polyether polyol or a polymer polyol. Polyether polyols of the type contemplated are those prepared by reacting a low molecular weight polyfunctional alcohol e.g. glycerol, trimethyolpropane, 1,2,6-hexanetriol, pentaerythritol, sorbitol or sucrose, with one or more alkylene oxides. The alkylene oxides are preferably lower alkylene oxides for example, ethylene oxide, propylene oxide, butylene oxide or mixtures thereof. Polyether polyols produced by this method can be made with a range of physical and chemical properties depending upon the degree of polymerisation, the relative proportions of the different alkylene oxides in the polyether part of the molecule etc and the particular alkylene oxides used. Polymer polyols which comprise a polyether polyol onto which has been grafted a vinyl polymer or copolymer (e.g. styrene/acrylonitrile) have been described in detail in for example GB 1412797 and EP 137723.

As mentioned above, the polyol is one having an average functionality in the range 2 to 6, preferably 2 to 3.5, and in which less than 20% of the hydroxyl groups are primary hydroxyl groups. It is also preferable that the molecular weight of the polyol is in the range 1500 to 8000.

The isocyanate composition used is one which contains toluene diisocyanate (TDI). The toluene diisocyanate, which typically exists as a mixture of isomers, may be present as such, in the form of a prepolymer with the polyol or mixed with other polyfunctional isocyanates, e.g. MDI. In general the relative proportions of isocyanate composition and polyol should be such as to produce an isocyanate:polyol ratio of between 0.8 and 1.2, preferably 0.9 and 1.1 when calculated on an equivalent basis.

As the polyurethane foaming reaction is base catalysed the reaction is suitably carried out in the presence of a base catalyst. The base catalyst may be any one of a wide range of inorganic or organic bases. Particularly suitable examples of catalysts include tertiary amines e.g. tributylamine, N-methylmorpholine, DABCO, TBD, 1,3-propanediamine and organic tin compounds e.g. tin (II) alkoxides tin (II) carboxylates, dialkyl tin salts of carboxylic acids or hydrohalic acids.

Other catalysts, for example derivatives of lead, antimony, titanium and mercury which are not so widely used in industry can also be used.

The amounts of such catalyst which are to be used will be familiar to the skilled man.

In order to produce a foam it is necessary to have present during the polyurethane forming reaction a blowing agent. Preferably the blowing agent is either water or a fluorocarbon blowing agent such as dichlorodifluoromethane, 1,1-dichloro-1-fluoroethane, 1-chloro-1,1-difluoroethane or 2,2-dichloroethane. The amount of blowing agent required will vary according to the density of the foam which is desired. Suitable levels of blowing agent will be familiar to the skilled man.

In manufacturing the flexible polyurethane foam, the components of the foam formulation are mixed and the resulting formulation allowed to foam. The fully risen foam is then cured at a temperature of between 130-150°C.

The present invention is now further described with reference to the following Examples.

A series of polyurethane foam formulations were prepared having the following compositions:

Polyol U 10.01 (ex BP)	- 100 parts
Water	- 4.7 parts
A-1 catalyst (ex BP)	- 0.1 parts
SO catalyst	- 0.2 parts
U-11 - fluorcarbon	- 0.2 parts
Silicone surfactant	- 1.0 parts

Each foam formulation was allowed to cream and rise. The risen foam was cured under standard conditions. When fully cured the breathability of each was measured using the apparatus in Figure 1.

Breathability Test

A cut sample of the foam (5 cm x 5 cm x 2.5 cm) was mounted in the top of the vacuum chamber. Using one of the

three flowmeters air was blown through the foam to the outside. The flow of air was in each case adjusted so that the manometer recorded a pressure of 0.25 mm of water across the 1.27 cm thickness of sample. The Table shows the flow rates obtained in cubic feet per minute.

In the Table the silicone surfactants are as follows.

A : $(CH_3)_3SiO(Si(CH_3)_2O)_{72}(Si(CH_3)(C_3H_6(OC_2H_4)_{22}(OC_3H_6)_{22}\ (OCH_3))O)_{5\ 5}Si(CH_3)_3$

B : 90% A
10% $(CH_3)_3SiO(Si(CH_3)_2O)_7(Si(CH_3)R^2O)_2Si(CH_3)_3$ (R^2 = allylphenol)

C : 90% A
10% $(CH_3)_3SiO(Si(CH_3)_2O)_7(Si(CH_3)R_2O)_2Si(CH_3)_3$ (R^2 = methoxyeugenol)

D : 90% A
10% $(CH_3)_3SiO(Si(CH_3)_2O)_8(Si(CH_3)R^2O)Si(CH_3)_3$ (R^2 = methoxyeugenol)

E : 90% A
10% $(CH_3)_3SiO(Si(CH_3)_2O)_7(Si(CH_3)R^2)_2Si(CH_3)_3$ (R^2 = eugenol)

Example	Foam Breathability (cubic feet/minute)
A	2.0
B	3.5
C	5.5
D	5.0
E	3.9

Although the R^2 groups are termed allylphenol, methoxyeugenol, and eugenol for convenience it will be obvious to the skilled man that the R^2 groups are infact the moiety obtained when such a species is reacted with a Si-H bond.

Claims

1. A process for preparing flexible polyurethane foam, which process comprises reacting and foaming a foam formulation comprising:

(1) a polyol selected from the group consisting of polyether polyols and polymer polyols, wherein the polyol is one having an average functionality in the range 2 to 6 and in which less than 20% of the hydroxyl groups are primary hydroxyl groups,
(2) an isocyanate composition containing toluene diisocyanate,
(3) a catalyst for the polyurethane forming reaction, and
(4) a blowing agent,
characterized in that the foam formulation further comprises a silicone surfactant composition which comprises a mixture of

(a) between 5 and 20 wt % of a lower molecular weight silicone surfactant having the formula

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_x(Si(CH_3)(R^2)O)_ySi(R^1)_3$$

wherein

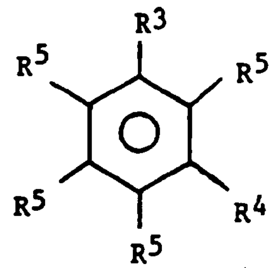
(i) x and y are such that

$$x+y = 2 - 10$$

and

$$\frac{y}{x+y} = 0.1 - 0.5$$

(ii) the R^1 groups are independently selected from C_1 to C_{10} hydrocarbyl groups
(iii) the R^2 group are independently selected from groups having the generic formula



wherein R^3 is a divalent hydrocarbyl group; R^4 is a polar moiety selected from the group consisting of -OH, $-NH_2$, Cl, -Br, and $-CH_2OH$, and the R^5 groups are independently selected from hydrogen or C_1 to C_{10} alkyl or alkoxy groups; and

(b) between 95 and 80 wt % of a high molecular weight silicone surfactant having the formula

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_p(Si(CH_3)(R^6)O)_qSi(R^1)_3$$

(i) p = 40 - 150
(ii) q = 3 - 15
(iii) R^6 is an ethylene oxide/propylene oxide copolymer having a molecular weight in the range 1500 - 5000 capped with alkoxy at one end and bound to silicon by a divalent hydrocarbyl group;

the molecular weight of the high molecular weight silicone surfactant being in the range 10,000 to 50,000.

2. The process of claim 1 wherein in said low molecular weight surfactant, R^1 is methyl, and x+y is 6 - 10.

3. The process of claim 1 wherein in said low molecular weight surfactant, R^4 is -OH or $-CH_2OH$.

4. The process of claim 1 wherein in said high molecular weight surfactant, R^1 is methyl, p is in the range 60 - 80, and q is in the range 5 - 9.

Patentansprüche

1. Verfahren zur Herstellung eines flexiblen Polyurethanschaums, umfassend das Reagieren und Schäumen einer Schaumkonfektionierung enthaltend:

(1) ein Polyol aus der Gruppe der Polyetherpolyole und Polymerpolyole, wobei das Polyol eines ist, das eine durchschnittliche Funktionalität im Bereich von 2 bis 6 hat und bei dem weniger als 20% der Hydroxylgruppen primäre Hydroxylgruppen sind,
(2) eine Isocyanatzusammensetzung, die Tolyol-Diisocyanat enthält,
(3) einen Katalysator für die Reaktion zur Bildung des Polyurethans, und
(4) ein Blähmittel,
dadurch **gekennzeichnet,** daß die Schaumkonfektionierung ferner eine oberflächenaktive Silikonzusammensetzung enthält, umfassend eine Mischung von

(a) zwischen 5 und 20 Gew% eines Silikontensids mit niedrigem Molekulargewicht mit der Formel

$$(R^1)_3SiO(Si(CH_3)\ (R^1)O)_x(Si(CH_3)\ (R^2)O)_ySi(R^1)_3$$

wobei

(i) x und y derart sind, daß

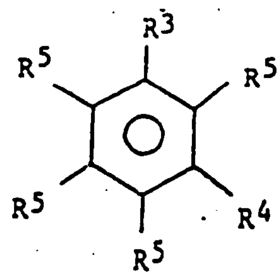
$$x + y = 2 - 10$$

und

$$\frac{y}{x+y} = 0.1 - 0.5$$

(ii) die R^1-Gruppen unabhängig voneinander aus C_1 bis C_{10} Hydrocarbylgruppen ausgewählt sind,

(iii) die R^2-Gruppen unabhängig voneinander ausgewählt sind aus Gruppen mit der allgemeinen Formel



in der R^3 eine divalente Hydrocarbylgruppe, R^4 ein polarer Rest, der aus der Gruppe bestehend aus -OH, $-NH_2$, Cl, -Br und $-CH_2OH$ ausgewählt ist, und die R^5-Gruppen unabhängig aus Wasserstoff oder C_1 bis C_{10} Alkyl- oder Alkoxygruppen ausgewählt sind; und

(b) zwischen 95 und 80 Gew% eines Silikontensids mit hohem Molekulargewicht mit der Formel

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_p(Si(CH_3)(R^6)O)_qSi(R^1)_3$$

wobei

(i) p = 40 - 150
(ii) q = 3 - 15
(iii) R^6 ein Ethylenoxid/Propylenoxid-Copolymer ist mit einem Molekulargewicht im Bereich von 1500 bis 5000, das an einem Ende mit Alkoxy abgeschlossen und durch eine divalente Hydrocarbylgruppe an Silizium gebunden ist;

wobei das Molekulargewicht des Silikontensids mit hohem Molekulargewicht im Bereich von 10.000 bis 50.000 liegt.

2. Verfahren nach Anspruch 1, bei dem in dem Tensid mit niedrigem Molekulargewicht R^1 Methyl ist und x+y 6 - 10 beträgt.

3. Verfahren nach Anspruch 1, bei dem R^4 in dem Tensid mit niedrigem Molekulargewicht -OH oder $-CH_2OH$ ist.

4. Verfahren nach Anspruch 1, bei dem in dem Tensid mit hohem Molekulargewicht R^1 Methyl ist, p im Bereich 60 - 80 liegt und q im Bereich 5 - 9 liegt.

Revendications

1. Procédé de fabrication d'une mousse de polyuréthanne souple ou flexible, conformément auquel on fait réagir et mousser ou s'expanser une composition de moussage qui comprend :

(1) un polyol choisi dans le groupe formé par les polyétherpolyols et les polyols polymériques, où le polyol en est un qui possède une fonctionnalité moyenne qui varie de 2 à 6 et dans lequel moins de 20% des radicaux hydroxyle sont des groupes hydroxyle primaires,
(2) une composition d'isocyanate contenant du diisocyanate de toluène,
(3) un catalyseur pour la réaction de formation du polyuréthanne et
(4) un agent porogène,
caractérisé en ce que la composition de moussage comprend, en outre, une composition de surfactif à base de silicone, qui est constituée d'un mélange

(a) de 5 à 20% en poids d'un surfactif à base de silicone d'un faible poids moléculaire répondant à la formule suivante

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_x(Si(CH_3)(R^2)O)_ySi(R^1)_3$$

dans laquelle

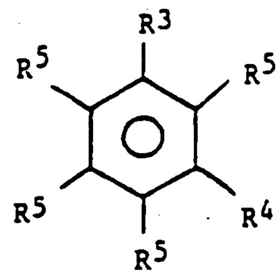
(i) x et y sont tels que

$$x+y = 2 - 10$$

et

$$\frac{y}{x+y} = 0,1 - 0,5$$

(ii) les symboles R^1 représentent, indépendamment, des radicaux hydrocarbyle en C_1 à C_{10},
(iii) le symbole R^2 représente, indépendamment, des radicaux répondant à la formule générique suivante :



dans laquelle R^3 représente un radical hydrocarbyle bivalent, R^4 représente un radical polaire choisi dans le groupe constitué de -OH, $-NH_2$, -Cl, -Br et $-CH_2OH$ et les symboles R^5 représentent, indépendamment, des atomes d'hydrogène ou des radicaux alcoxy ou alkyle en C_1 à C_{10} et

(b) de 95 à 80% en poids d'un surfactif à base de silicone de poids moléculaire élevé, répondant à la formule suivante :

$$(R^1)_3SiO(Si(CH_3)(R^1)O)_p(Si(CH_3)(R^6)O)_qSi(R^1)_3$$

dans laquelle

(i) p = 40 - 150
(ii) q = 3 - 15
(iii) le symbole R^6 représente un copolymère d'oxyde d'éthylène/oxyde de propylène possédant un poids moléculaire variant de 1500 à 5000 coiffé de groupes alcoxy à l'une de ses extrémités et lié à du silicium par un radical hydrocarbyle bivalent,

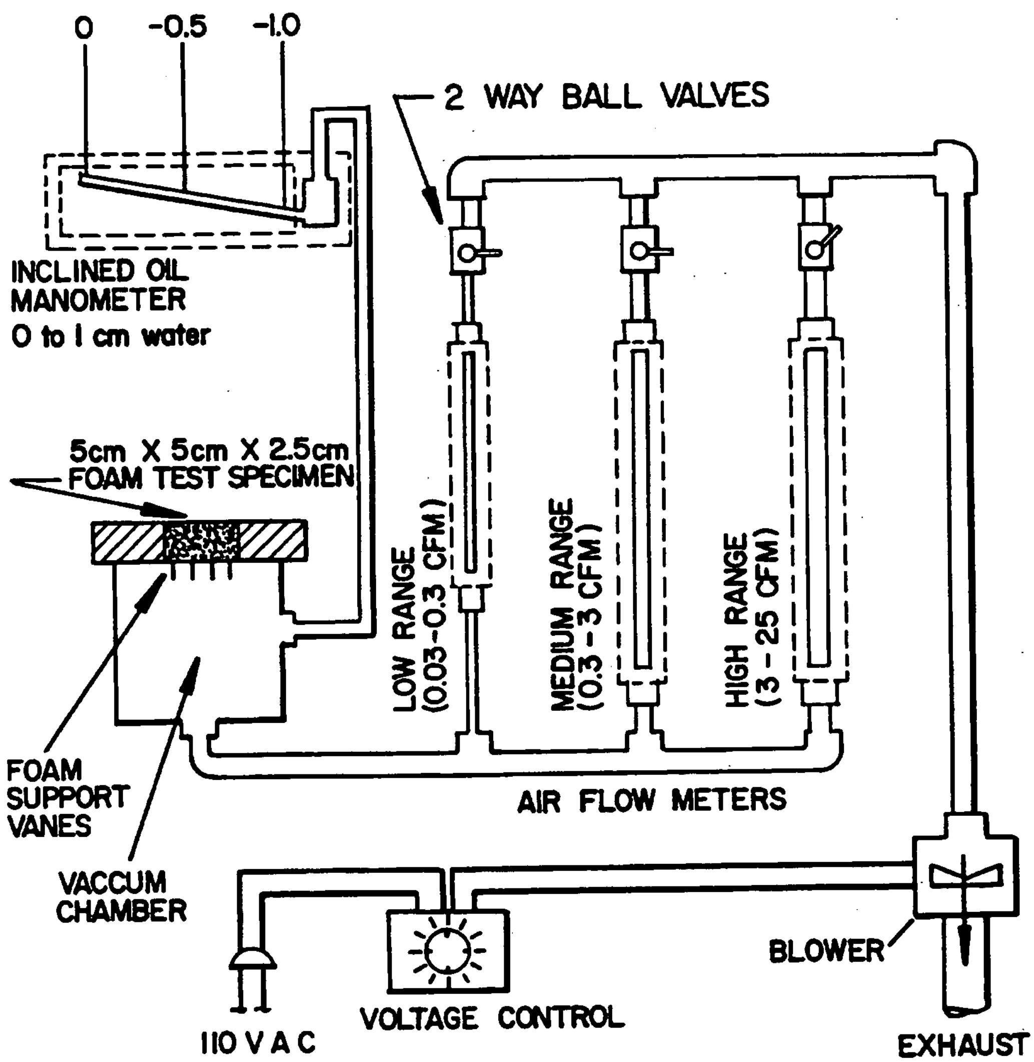
le poids moléculaire du surfactif à base de silicone de poids moléculaire élevé fluctuant dans la plage de 10.000 à 50.000.

2. Procédé suivant la revendication 1, caractérisé en ce que dans le surfactif de faible poids moléculaire précité, R^1 représente le radical méthyle et x+y varie de 6 à 10.

3. Procédé suivant la revendication 1, caractérisé en ce que dans le surfactif de faible poids moléculaire précité, R^4 représente le radical -OH ou $-CH_2OH$.

4. Procédé suivant la revendication 1, caractérisé en ce que dans le surfactif de poids moléculaire élevé précité, R^1 représente le radical méthyle, p varie de 60 à 80 et q varie de 5 à 9.

F I G. 1


0
-0.5
-1.0
2 WAY BALL VALVES
INCLINED OIL MANOMETER
0 to 1 cm water
5cm X 5cm X 2.5cm FOAM TEST SPECIMEN
LOW RANGE (0.03-0.3 CFM)
MEDIUM RANGE (0.3 - 3 CFM)
HIGH RANGE (3 - 25 CFM)
FOAM SUPPORT VANES
VACCUM CHAMBER
AIR FLOW METERS
BLOWER
110 V A C
VOLTAGE CONTROL
EXHAUST